Supporting Information

Experimental Section

^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer using the residual proton resonance of the solvent as the internal standard. Chemical shifts are reported in parts per million (ppm). ^{13}C NMR spectra were proton decoupled and recorded on a 100 MHz NMR spectrometer using the carbon signal of the deuterated solvent as the internal standard. EI mass spectra were obtained at the Molecular Weight Characterization Facility at University of Massachusetts, Amherst. Analytical thin layer chromatography was performed on silica plates with F-254 indicator and visualization was accomplished by UV lamp. All chemicals were obtained from commercial sources and used as received, unless otherwise mentioned. Rat anti-DNP IgG protein was purchased from Invitrogen. Synthetic procedures and characterization data for all the compounds are given in Supporting Information. Fluorescence intensity values were recorded at 620 nm for Nile red on JASCO FP-6500 spectrofluorimeter and Molecular Devices SpectraMax M5 micro plate reader with excitation at 550 nm.

Sample preparation for micelle and protein studies

The stock solutions for the micelle and protein binding studies were prepared by dissolving the dendrons in MilliQ water. Excess of Nile red was added to aqueous solution of these dendrons, and stirred at 5 °C for 12 h. Then the solution was filtered through a 0.22 μm filter.

Guest release studies

Solutions of Nile red encapsulated **G1-DNP** and **G2-DNP** dendrons were incubated with 7.5 μM protein solutions in 5 mM Phosphate buffer. Fluorescence intensities of these solutions at 620 nm were monitored for 12 h and the changes in emission intensities of the Nile red were used to calculate the percentage dye release.

Dynamic light-scattering (DLS) experiments

Size distributions of the micelles were determined by Nano series Nano-ZS (Malvern Instrument) Zetasizer. The dendron solutions were filtered through a 0.22 μm filter to eliminate dust before each measurement. The temperature was kept constant at 25 °C. Solutions of **G1-DNP** and **G2-DNP** dendrons were incubated with 7.5 μM protein solutions for 1 h in 5 mM Phosphate buffer before the DLS measurements were performed.

Determination of Critical Aggregation Concentrations (CACs)

The emission spectra of Nile Red at different dendron concentrations were used to calculate the critical aggregation concentrations (CACs) of the dendrons. Plotting the emission intensity of Nile red as a function of dendron concentration affords an inflection point, which is taken to be

that dendron's CAC (Figure S1). Using this method, CACs for **G1-DNP** and **G2-DNP** dendrons were found to be 0.035 mg/ml (18 μM) and 0.020 mg/ml (5 μM), respectively.

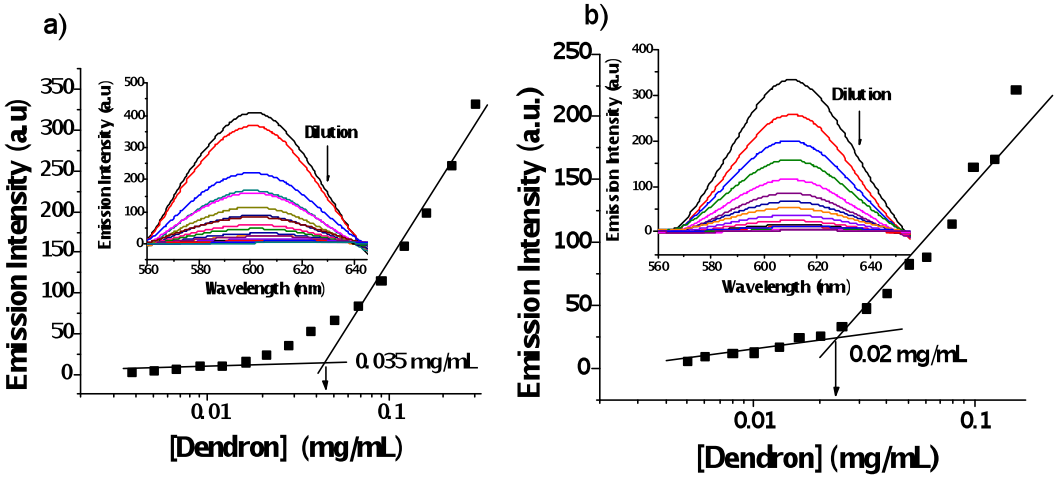
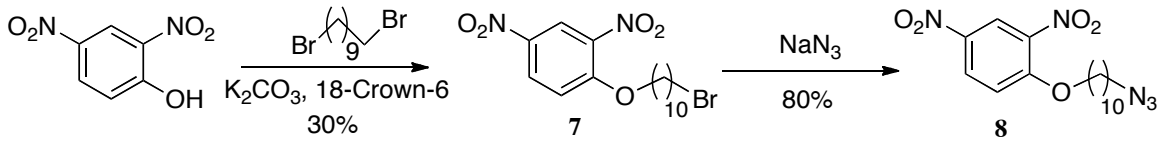


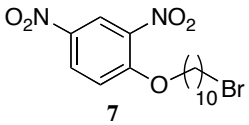
Figure S1. CAC plots of a) **G1-DNP** and b) **G2-DNP** dendrons. Insets show the emission intensity of Nile red at different dendron concentrations.

Synthesis:

Synthesis of dinitrophenyl ligand **8**



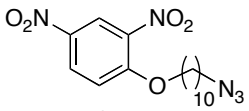
Synthesis of compound **7**



To a solution of 2,4-Dinitrophenol (5 g, 0.027 mol, 1 equiv) and 1,10-Dibromodecane (24.3 mL, 0.1 mol, 4 equiv) in dry acetone was added K_2CO_3 (7.45 g, 0.051 mol, 2 equiv) and 18-crown-6 (0.7 g, 0.0027 mol, 0.1 equiv). The resulting reaction mixture was refluxed under argon atmosphere for 12 h. Product formation was confirmed by TLC; the reaction mixture was partitioned between ethyl acetate and water. The aqueous layer was extracted twice with ethyl acetate and the combined organic layers were dried over Na_2SO_4 and evaporated to dryness. The crude product was purified with automated flash chromatography by using ethyl acetate/hexane

solvent system to yield 3.2 g (30%) of pure compound **7**. ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 8.74 (d, J = 2.76 Hz, 1H), 8.40-8.43 (dd, J = 9.26 Hz, 2.80 Hz, 1H), 7.20 (d, J = 9.29 Hz, 1H), 4.23 (t, J = 6.39 Hz, 2H), 3.41 (t, J = 6.85 Hz, 2H), 1.82-1.92 (m, 4H), 1.30-1.60 (m, 12H); ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 156.9, 139.8, 138.9, 129.0, 121.8, 114.2, 70.9, 34.1, 32.8, 29.3, 29.3, 29.1, 28.7, 28.6, 28.1, 25.7; EI-MS *m/z* calculated for $C_{16}H_{23}BrN_2O_5$ 404.08; found: 404.28.

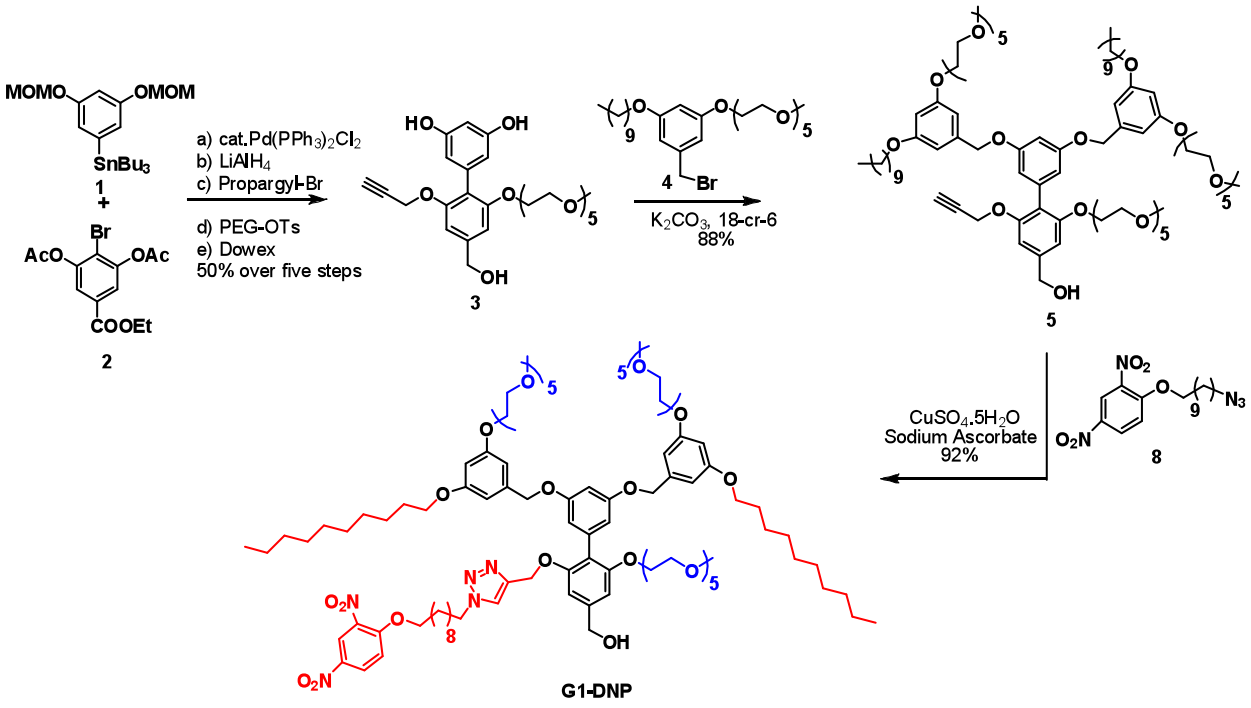
Synthesis of compound **8**



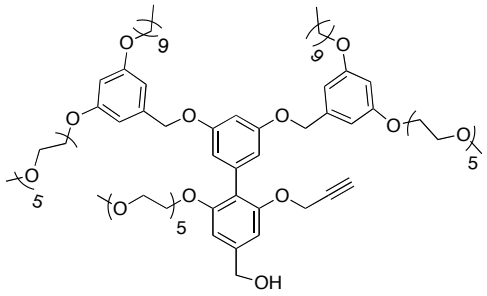
8

To a solution of **7** (3 g, 7.44 mmol, 1 equiv) in dry DMF (25 mL), NaN_3 (2.9 g, 44.64 mmol, 6 equiv) was added and heated at 60 ^{o}C for 12 h. Product formation was confirmed by using TLC. The reaction mixture was partitioned between ethyl acetate and water mixture. The aqueous layer was extracted twice with ethyl acetate and the combined organic layers were dried over Na_2SO_4 and evaporated to dryness. The crude product was purified with automated flash chromatography by using ethyl acetate/hexane solvent system to yield 2.3 g (85%) of pure compound **8**. ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 8.73 (d, J = 2.82 Hz, 1H), 8.39-8.43 (dd, J = 9.26, 2.80 Hz, 1H), 7.17-7.19 (d, J = 9.31 Hz, 1H), 4.21-4.24 (t, J = 6.38 Hz, 2H), 4.23-4.27 (t, J = 6.94 Hz, 2H), 1.84-1.91 (m, 2H), 1.30-1.61 (m, 14H); ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 156.9, 139.8, 138.9, 129.0, 121.8, 114.2, 70.9, 63.1, 51.5, 32.8, 29.3, 29.1, 28.8, 28.6, 26.7, 25.7; HRMS (FAB+) calculated for $C_{16}H_{23}N_5O_5$ 365.17; found 366.17 (M+H).

Synthesis of G1-DNP dendron:



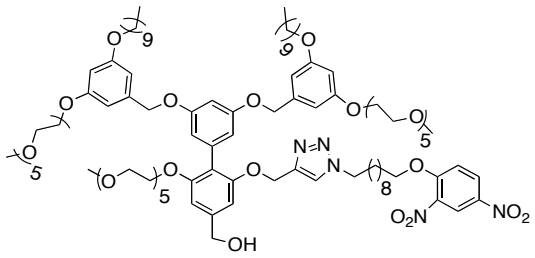
Synthesis of compound **5**



5

To a solution of biaryl monomer **3**[1] (0.15 g, 0.288 mmol, 1 equiv) and bromobenzyl compound **4**[2] (0.35 g, 0.60 mmol, 2.1 equiv) in dry acetone was added K_2CO_3 (0.16 g, 1.15 mmol, 4 equiv) and 18-Crown-6 (0.0076 g, 0.0288 mmoles, 0.1 equiv). The resulting reaction mixture was refluxed under Argon atmosphere for 12 h, while monitoring the progress of the reaction by TLC. After completion of the reaction, acetone was evaporated and the crude reaction mixture was partitioned between ethyl acetate and water. The aqueous layer was extracted twice with ethyl acetate and the combined organic layers were dried over Na_2SO_4 and evaporated to dryness. The crude product was purified with automated flash chromatography by using ethyl acetate/methanol solvent system to yield 0.38 g of pure compound **5** (yield: 88%). ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 6.76-6.78 (m, 2H), 6.56-6.61 (m, 7H), 6.40-6.41 (t, J = 2.24 Hz, 2H), 4.93 (s, 4H), 4.69 (s, 2H), 4.04-4.11 (m, 6H), 3.81-3.93 (m, 8H), 3.50-3.72 (m, 50H), 3.35-3.36 (m, 9H), 2.46-2.47 (t, J = 2.36 Hz, 1H), 1.71-1.78 (m, 4H), 1.26-1.46 (br, 28H), 0.85-.89 (t, J = 6.88 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 160.4, 160.0, 159.1, 157.1, 155.5, 142.2, 139.4, 135.5, 119.9, 110.2, 106.2, 105.7, 105.5, 105.0, 101.0, 100.8, 71.9, 71.9, 70.8, 70.6, 70.6, 70.5, 70.5, 70.5, 70.4, 70.4, 70.0, 69.7, 69.6, 68.8, 68.1, 67.4, 65.2, 59.0, 56.4, 31.9, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1; MALDI-ToF *m/z* 1536.89 ($C_{83}H_{132}O_{24}$+Na^+ requires 1536.91).

Synthesis of **G1-DNP**

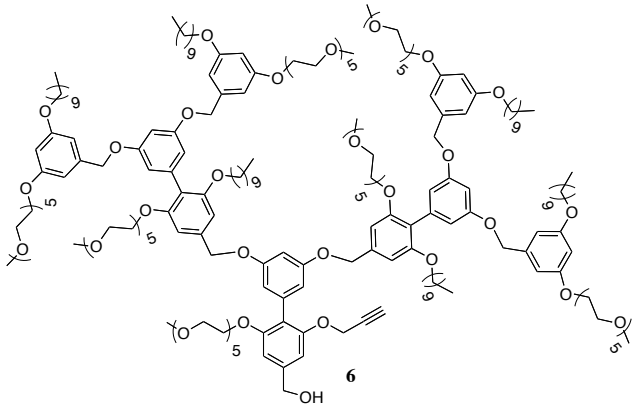


G1-DNP

To the mixture of dendritic propargyl compound **5** (0.05 g, 0.033 mmol, 1.0 equiv) and DNP-azide **8** (0.014 g, 0.039 mmol, 1.2 equiv) in a vial was added $CuSO_4$. $5H_2O$ (0.0016 g, 0.0066 mmol, 0.2 equiv.) and sodium ascorbate (0.0013 g, 0.0065 mmol, 0.2 equiv.) in THF/H_2O (1:1) solvent mixture. The resulting reaction mixture was stirred at RT for 24 h, while monitoring the progress of the reaction by TLC. After completion of the reaction, the reaction mixture was partitioned between ethyl acetate and saturated aqueous NH_4Cl solution. The aqueous layer was

extracted twice with ethyl acetate and the combined organic layers were dried over Na_2SO_4 and evaporated to dryness. . The crude product was purified with automated flash chromatography by using ethyl acetate/methanol solvent system to yield 0.057 g of pure **G1-DNP** (yield: 92 %). ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 8.71-8.72 (d, J = 2.75 Hz, 1H), 8.37-8.40 (dd, J = 9.24, 2.71 Hz, 1H), 7.15-7.26 (m, 1H), 6.38-6.77 (m, 12H), 4.68-5.13 (m, 8H), 4.05-4.20 (m, 8H), 3.81-3.93 (m, 8H) 3.51-3.70 (m, 50H), 3.51-3.62 (m, 9H), 1.71-1.76 (m, 10H), 1.22-1.44 (br, 40H), 0.85-0.88 (t, J = 6.68 Hz, 6H); ^{13}C (100 MHz, $CDCl_3$), δ (ppm): 160.4, 160.0, 159.0, 157.0, 156.9, 156.4, 142.5, 139.8, 139.8, 139.3, 135.9, 129.0, 121.8, 119.6, 114.2, 110.4, 106.2, 105.7, 105.6, 105.4, 105.2, 100.9, 100.8, 100.6, 71.92, 71.90, 70.8, 70.7, 70.6, 70.59, 70.56, 70.55, 70.49, 70.47, 70.44, 69.97, 69.68, 69.63, 68.79, 68.12, 67.44, 65.13, 59.03, 59.01, 50.25, 31.91, 30.0, 29.7, 29.6, 29.5, 29.4, 29.34, 29.30, 29.2, 29.1, 29.0, 28.8, 28.6, 26.3, 26.1, 25.6, 22.7, 14.1; MALDI-ToF *m/z* 1902.00 ($C_{99}H_{155}N_5O_{29}$+Na^+ requires 1902.31).

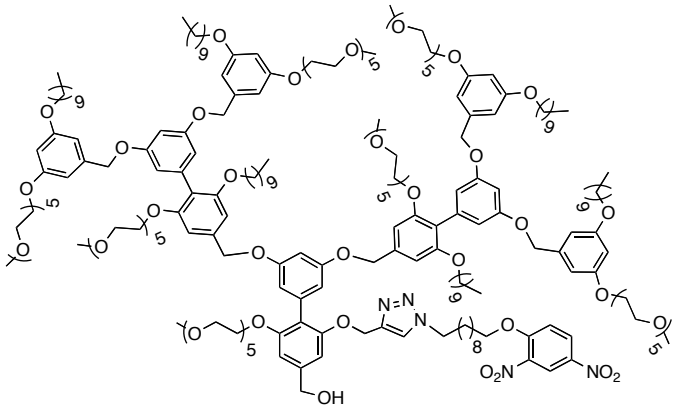
Synthesis of compound **6**



6

To the biaryl monomer core **3** (0.15 g, 0.288 mmoles, 1 equiv) and dendritic bromobenzyl compound **G1-Br** [2] (1.1 g, 0.65 mmol, 2.3 equiv) in dry acetone was added K_2CO_3 (0.15 g, 1.10 mmol, 4 equiv) and 18-Crown-6 (0.0074 g, 0.0288 mmoles, 0.1 equiv). The resulting reaction mixture was refluxed under Argon atmosphere for 24 h; progress of the reaction is monitored using TLC. After completion of the reaction, acetone was evaporated and the crude reaction mixture was partitioned between ethyl acetate and water. The aqueous layer was extracted twice with ethyl acetate and the combined organic layers were dried over Na_2SO_4 and evaporated to dryness. The crude product was purified with automated flash chromatography by using ethyl acetate/methanol solvent system to yield 0.8 g of pure compound **6** (yield: 75%). ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 6.57-6.80 (m, 24H), 6.40-6.42 (t, J = 2.25 Hz, 3H), 5.02 (s, 4H), 4.91 (s, 8H), 4.70 (s, 2H), 4.58-4.59 (d, J = 2.25 Hz, 2H), 4.04-4.12 (m, 14H), 3.82-3.93 (m, 20H), 3.50-3.73 (m, 118H), 3.34-3.36 (m, 21H), 2.48-2.49 (t, J = 2.25 Hz, 1H), 1.71-1.77 (m, 10H), 1.6-1.63 (m, 6H), 1.26-1.45 (br, 81H), 0.83-0.87 (m, 18H); ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 160.4, 160.0, 159.0, 157.3, 156.9, 139.3, 137.9, 135.9, 135.7, 119.8, 110.2, 106,2, 105,7, 100.8, 71.9, 71.8, 70.7, 70.6, 70.59, 70.57, 70.51, 70.46, 70.44, 70.43, 70.41, 69.9, 69.7, 68.8, 68.0, 67.4, 59.04, 59.01, 33.0, 29.63, 29.61, 29.60, 29.45, 29.35, 29.33, 29.30, 29.15, 26.1, 22.7, 22.6, 14.1; MALDI-ToF *m/z* 3739.84 ($C_{207}H_{332}O_{56}$+Na^+ requires 3739.82).

Synthesis of **G2-DNP**



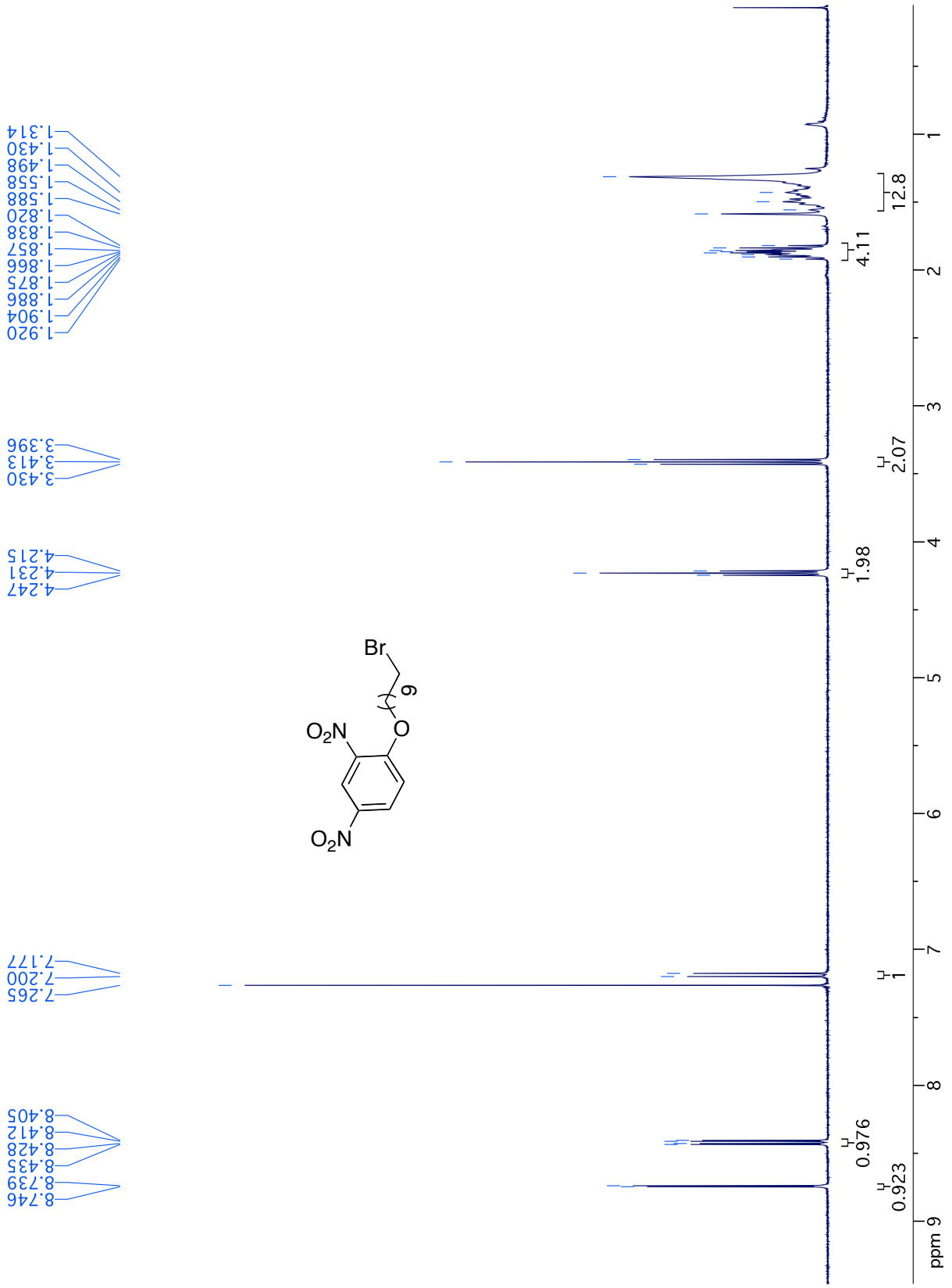
G2-DNP

To the mixture of dendritic propargyl compound **6** (0.03 g, 0.008 mmol, 1.0 equiv) and DNP-azide **8** (0.006 g, 0.016 mmol, 2.0 equiv) in a vial was added $CuSO_4$. $5H_2O$ (0.0039 g, 0.0016 mmol, 0.2 equiv.) and sodium ascorbate (0.00032 g, 0.0016 mmol, 0.2 equiv.) in THF/H_2O (1:1) solvent mixture. The resulting reaction mixture was stirred at RT for 24 h, while monitoring the progress of the reaction by TLC. After completion of the reaction, the reaction mixture was partitioned between ethyl acetate and saturated aqueous NH_4Cl solution. The aqueous layer was extracted twice with ethyl acetate and the combined organic layers were dried over Na_2SO_4 and evaporated to dryness. The crude product was purified with automated flash chromatography by using ethyl acetate/methanol solvent system to yield 0.02 g of pure **G2-DNP** (yield: 60 %). ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 8.67-8.68 (d, J = 2.85 Hz, 1H), 8.30-8.33 (dd, J = 9.24, 2.71 Hz, 1H), 7.06-7.09 (m, 1H), 6.55-6.73 (m, 24H), 6.40-6.41 (m, 4H), 4.91-5.00 (m, 14H), 4.69 (s, 2H), 3.48-4.11 (m, 154H), 3.33-3.36 (m, 21H), 1.60-1.77 (m, 20H), 1.26-1.46 (m, 95H), 0.83-0.88 (m, 18H); ^{13}C (100 MHz, $CDCl_3$), δ (ppm): 160.4, 160.0, 159.0, 157.3, 157.2, 157.0, 156.9, 156.8, 139.3, 135.8, 133.5, 129.0, 121.7, 119.8, 114.3, 110.28, 110.26, 106.2, 105.7, 100.7, 77.2, 71.93, 71.90, 70.8, 70.62, 70.61, 70.58, 70.52, 70.46, 7043, 70.42, 69.71, 68.10, 67.4, 59.04, 59.0, 31.9, 29.7, 29.64, 29.61, 29.60, 29.45, 29.34, 29.32, 29.31, 29.19, 26.12, 26.10, 22.70, 22.68, 14.15; MALDI-ToF *m/z* 4105.70 ($C_{223}H_{355}O_{61}$+Na^+ requires 4105.20).

References:

[1] M. A. Azagarsamy, P. Sokkalingam, S. Thayumanavan, *J. Am. Chem. Soc.* **2009**, *131*, 14184-14185.

[2] S. V. Aathimanikandan, E. N. Savariar, S. Thayumanavan, *J. Am. Chem. Soc.* **2005**, *127*, 14922-14929.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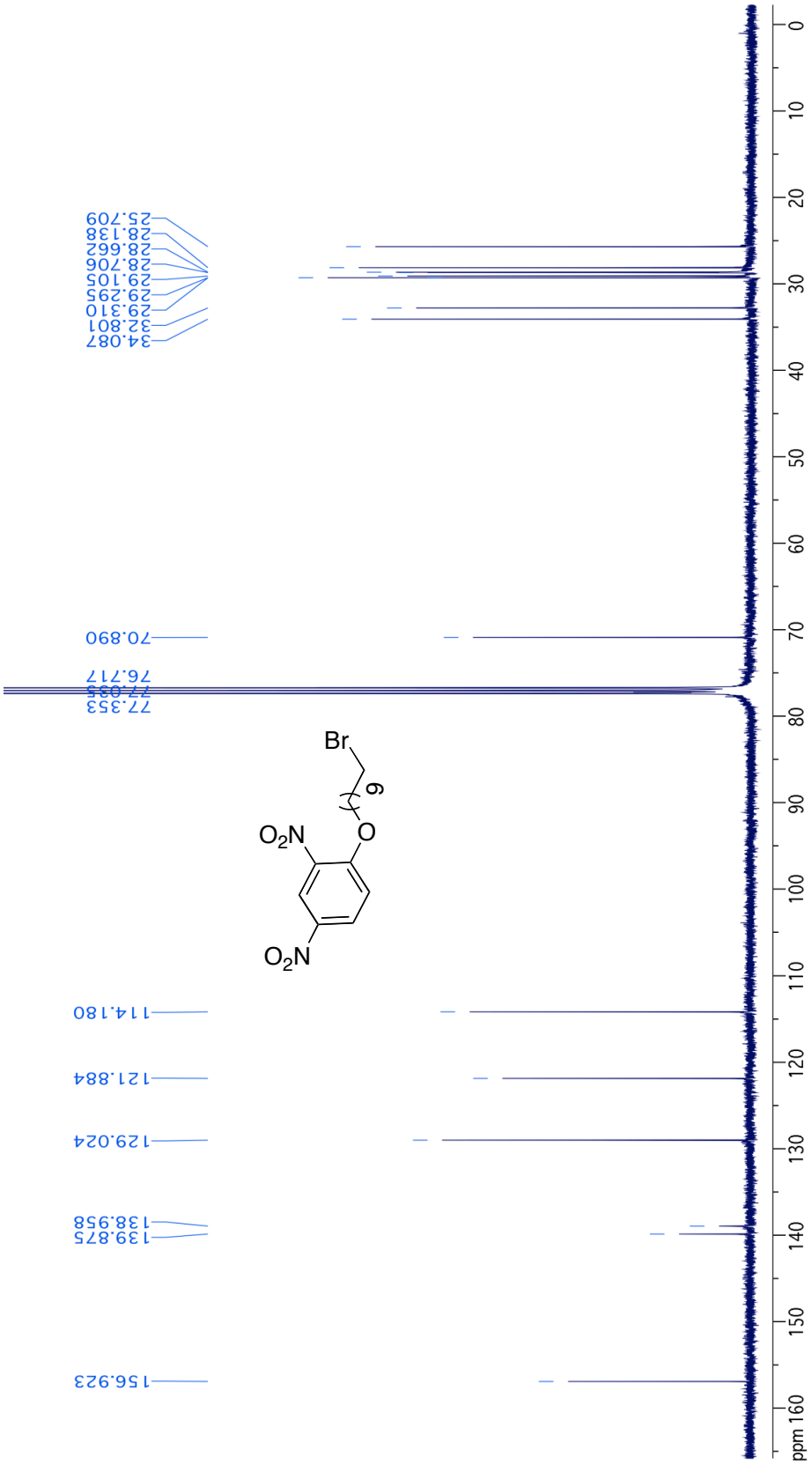
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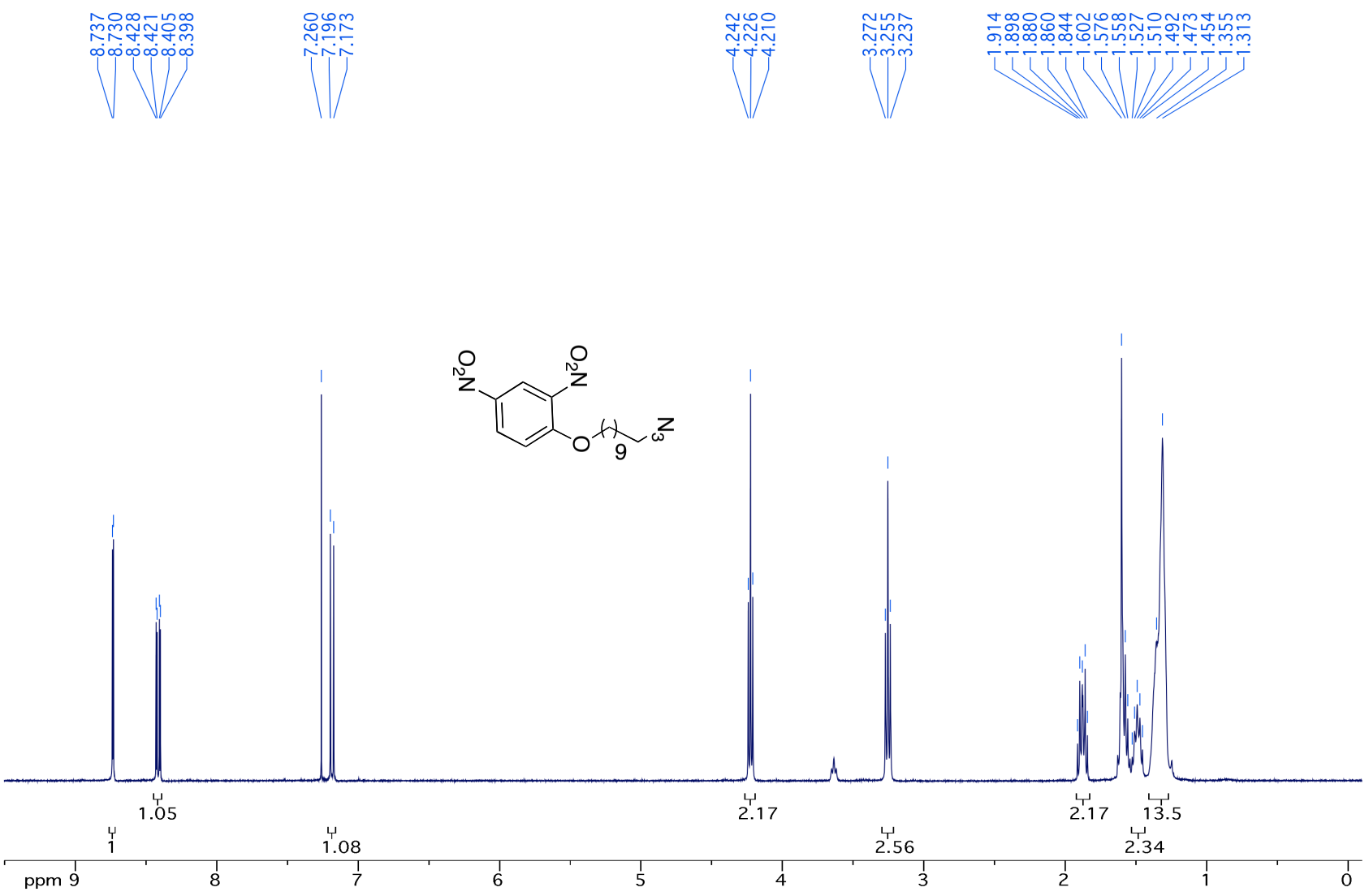
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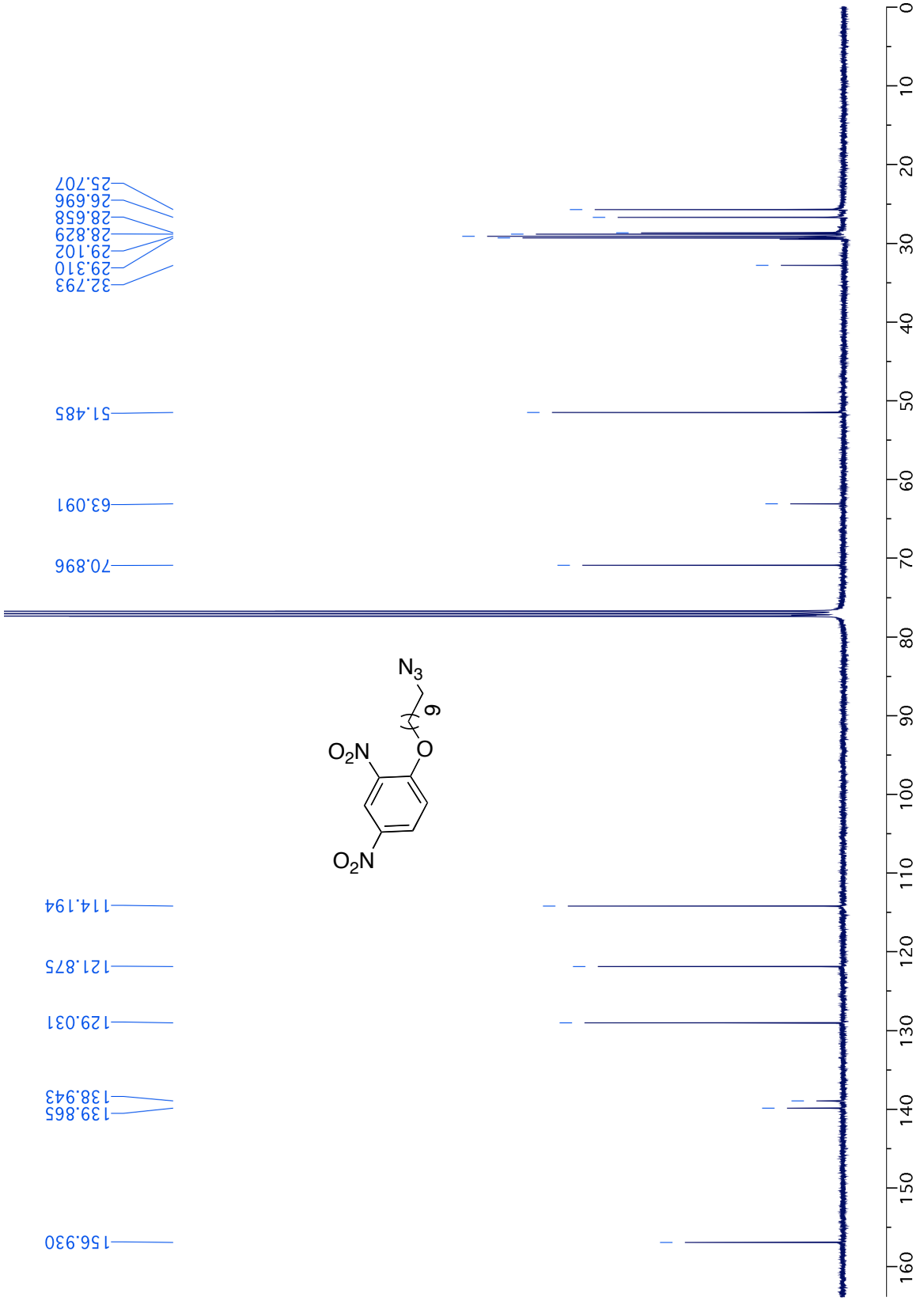
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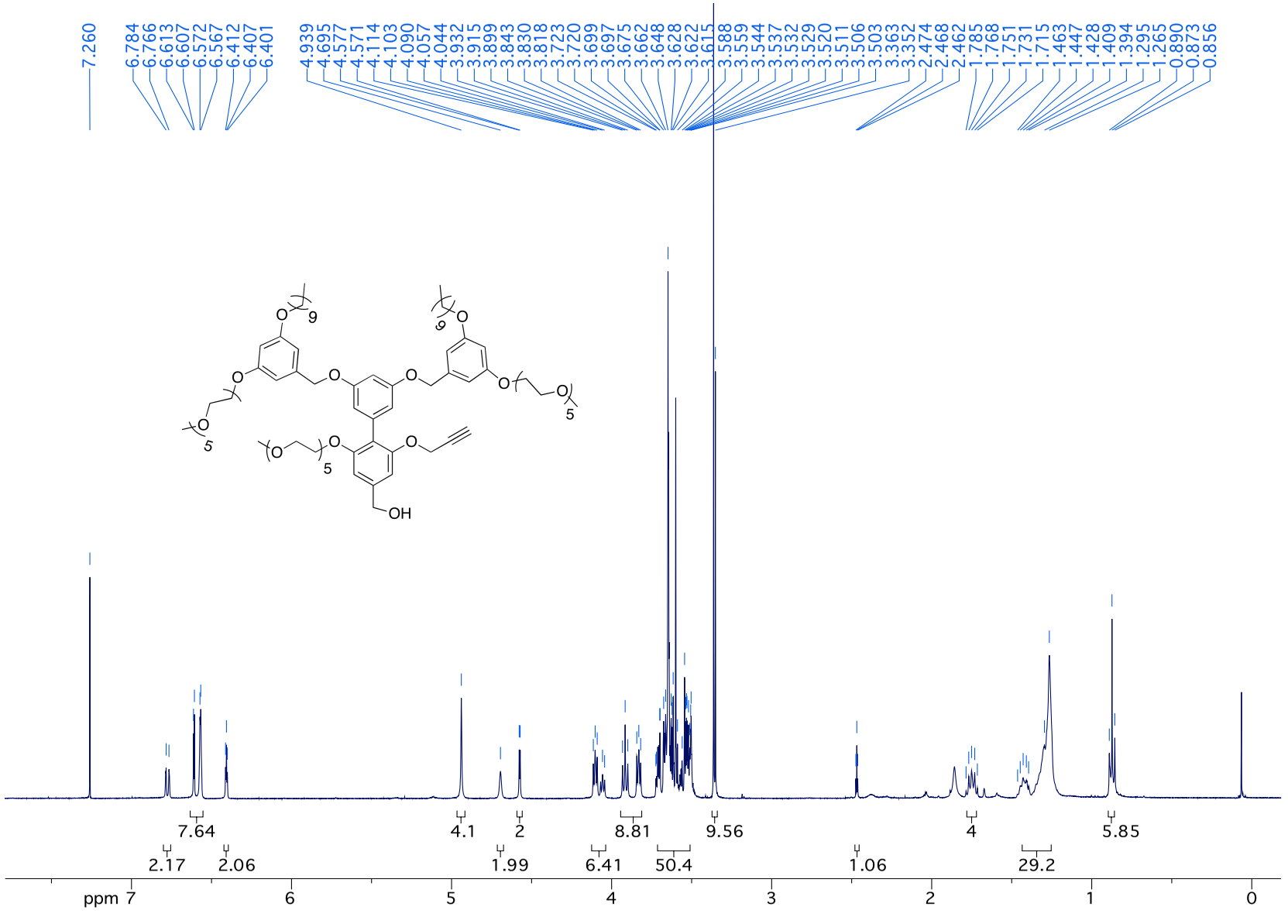
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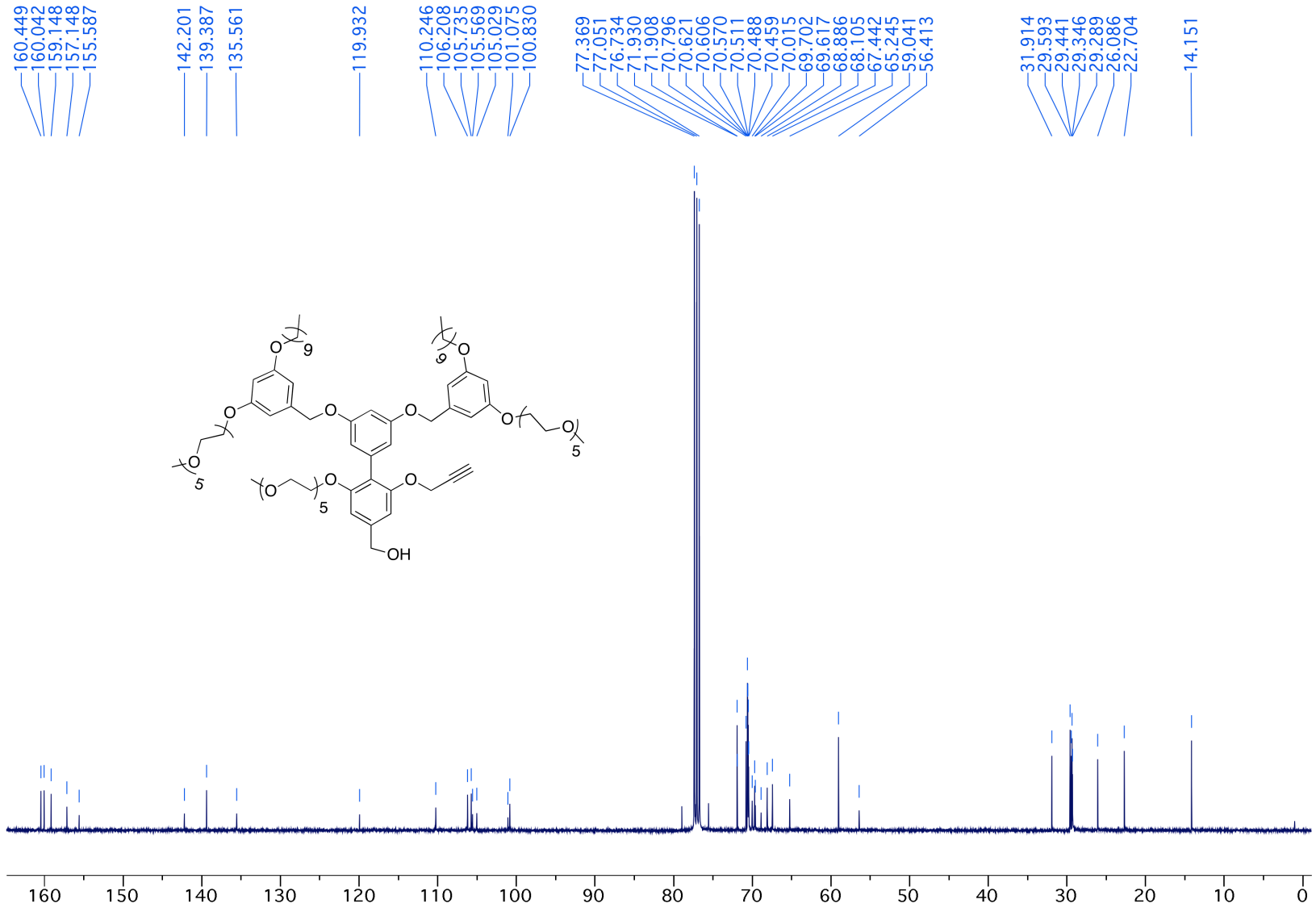
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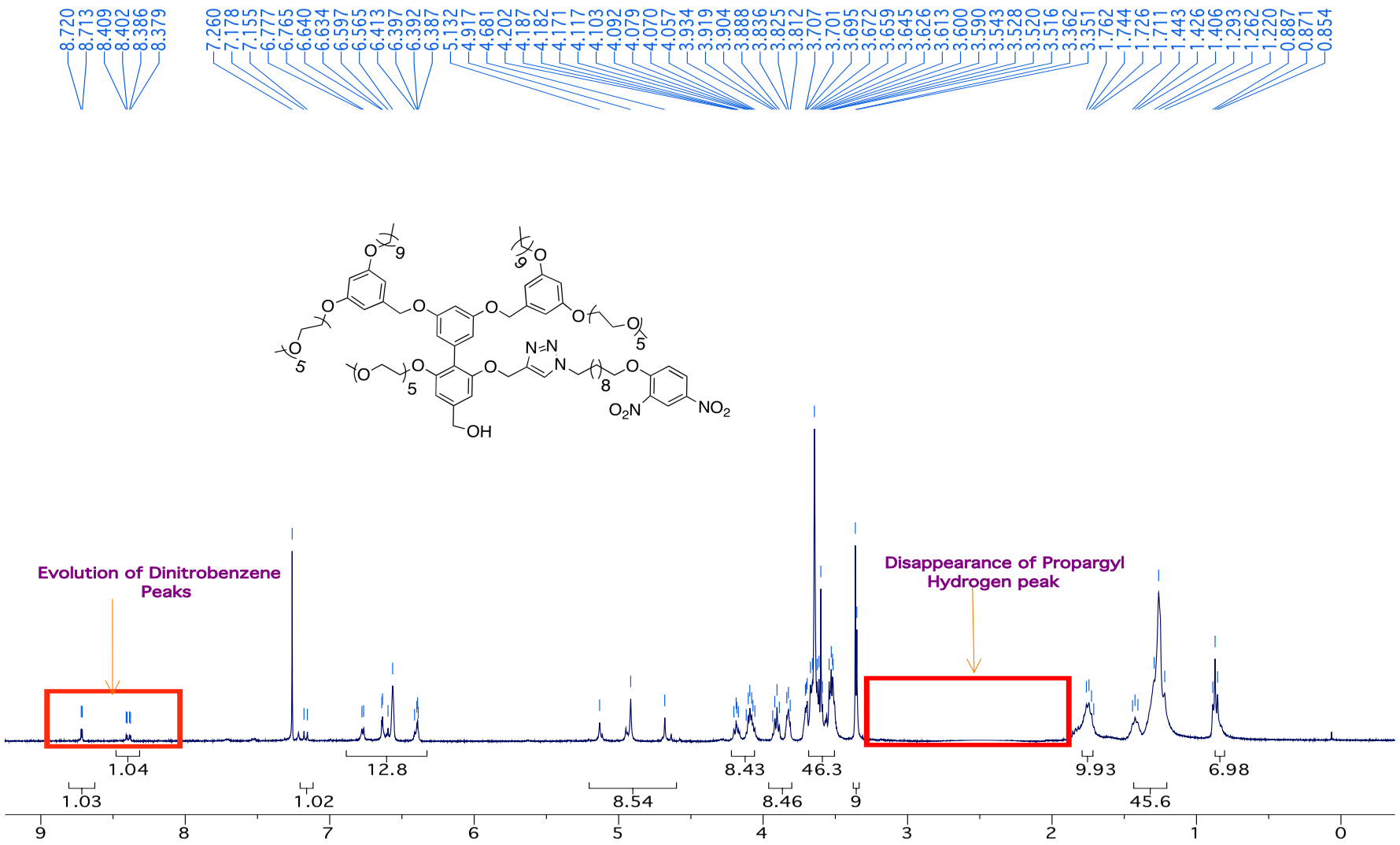
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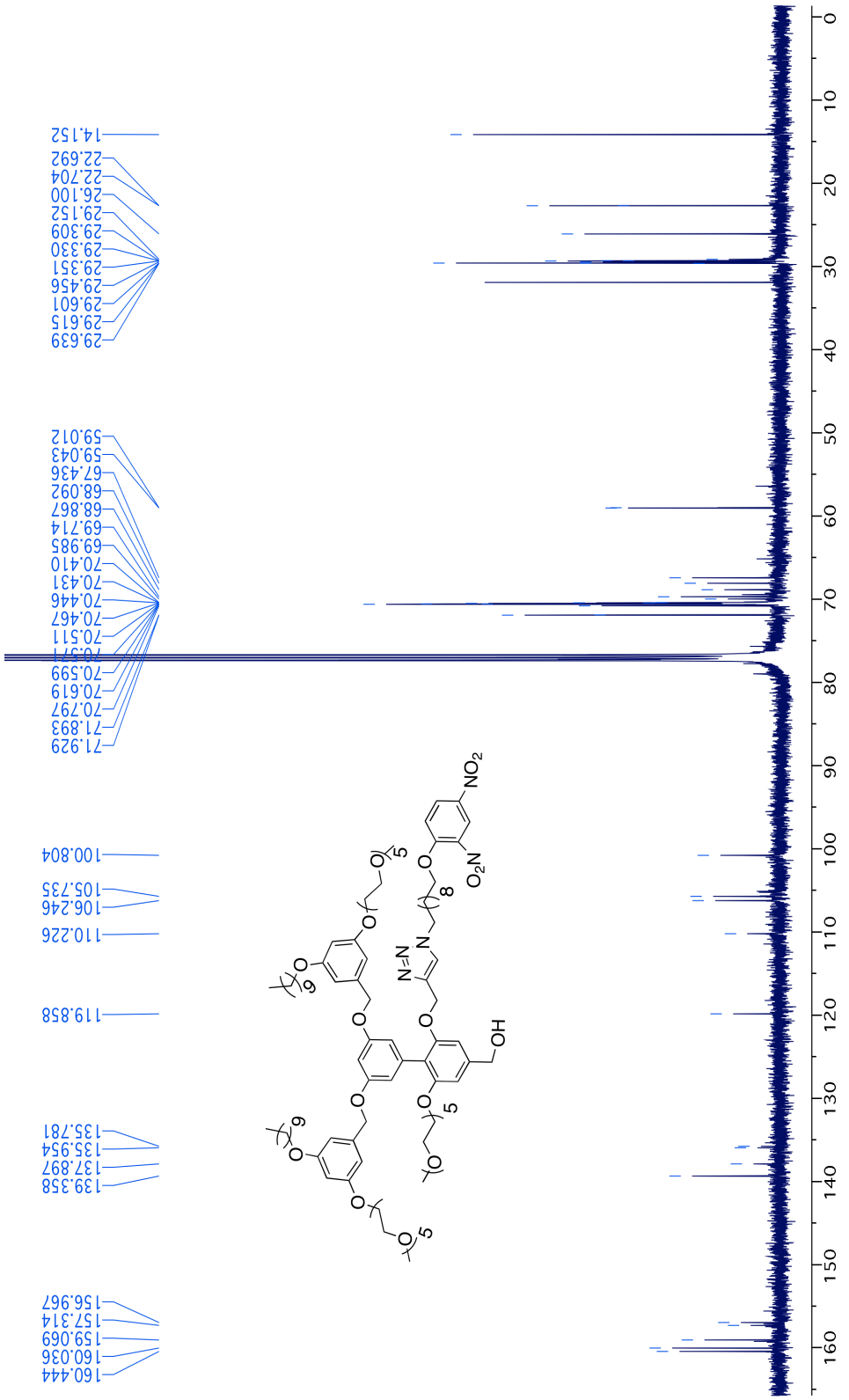
6.777
6.765
6.640
6.634
6.597
6.565
6.413
6.397
6.392
6.387
5.132
4.917
4.681
4.202
4.187
4.182
4.171
4.117
4.103
4.092
4.079
4.070
4.057
3.934
3.919
3.904
3.888
3.836
3.825
3.812
3.707
3.701
3.695
3.672
3.659
3.645
3.626
3.613
3.600
3.590
3.543
3.528
3.520
3.516
3.362
3.351
1.762
1.744
1.726
1.711
1.443
1.426
1.406
1.293
1.262
1.220
0.887
0.871
0.854
Evolution of Dinitrobenzene Peaks
Disappearance of Propargyl Hydrogen peak
1.04
12.8
8.43
46.3
9.93
6.98
1.03
1.02
8.54
8.46
9
45.6
9
8
7
6
5
4
3
2
1
0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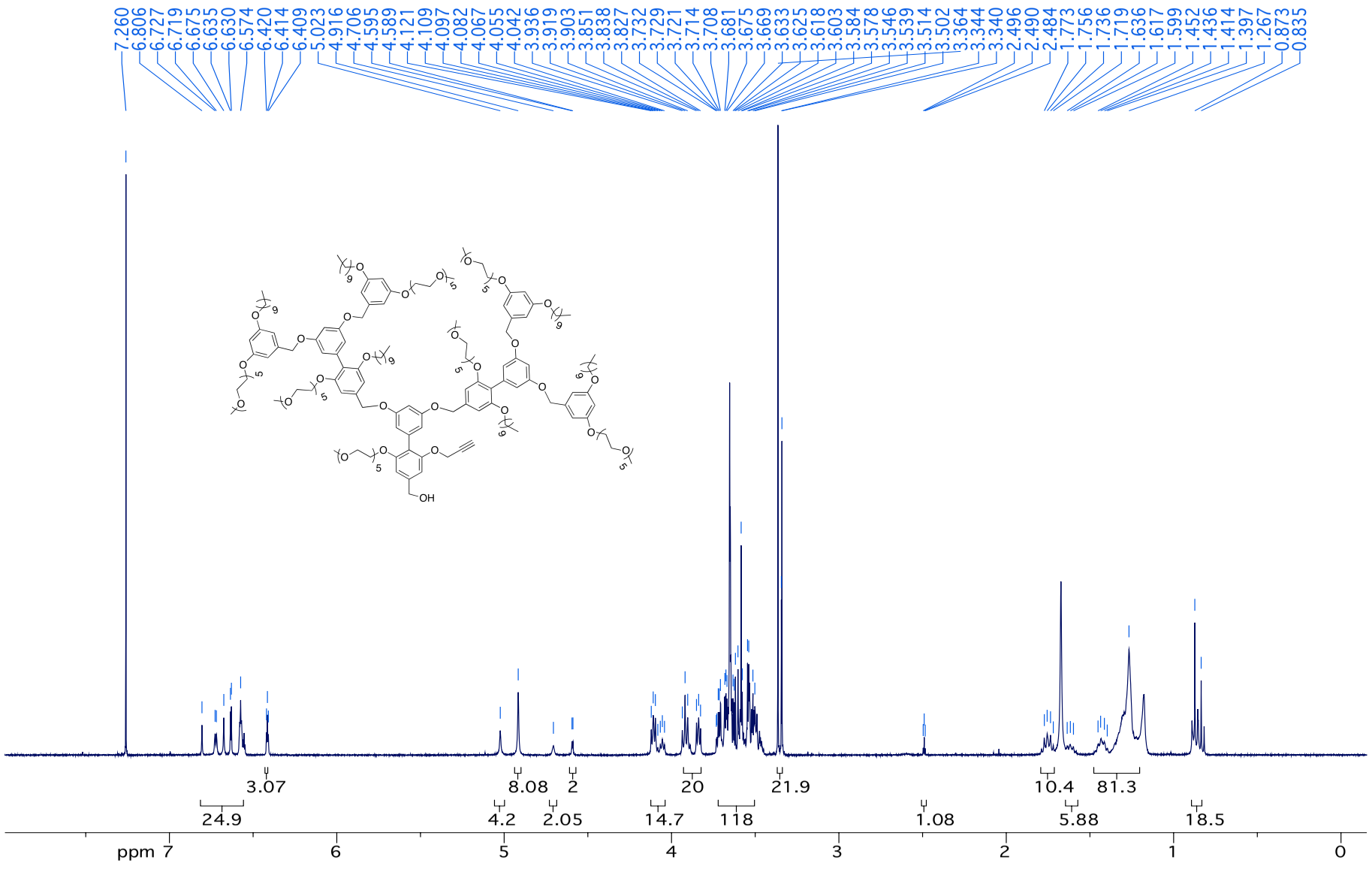
22.692
22.704
26.100
29.152
29.309
29.330
29.351
29.456
29.601
29.615
29.639
59.012
59.043
67.436
68.092
68.867
69.714
69.985
70.410
70.431
70.446
70.467
70.511
70.571
70.599
70.619
70.797
71.893
71.929
100.804
105.735
106.246
110.226
119.858
135.781
135.954
137.897
139.358
156.967
157.314
159.069
160.036
160.444
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
OH
NO_2
O_2N
N=N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6.806
6.727
6.719
6.675
6.635
6.630
6.574
6.420
6.414
6.409
5.023
4.916
4.706
4.595
4.589
4.121
4.109
4.097
4.082
4.067
4.055
4.042
3.936
3.919
3.903
3.851
3.838
3.827
3.732
3.729
3.721
3.714
3.708
3.681
3.675
3.669
3.633
3.625
3.618
3.603
3.584
3.578
3.546
3.539
3.514
3.502
3.364
3.344
3.340
2.496
2.490
2.484
1.773
1.756
1.736
1.719
1.636
1.617
1.599
1.452
1.436
1.414
1.397
1.267
0.873
0.835
OH
3.07
8.08
2
20
21.9
10.4
81.3
24.9
4.2
2.05
14.7
118
1.08
5.88
18.5
ppm 7
6
5
4
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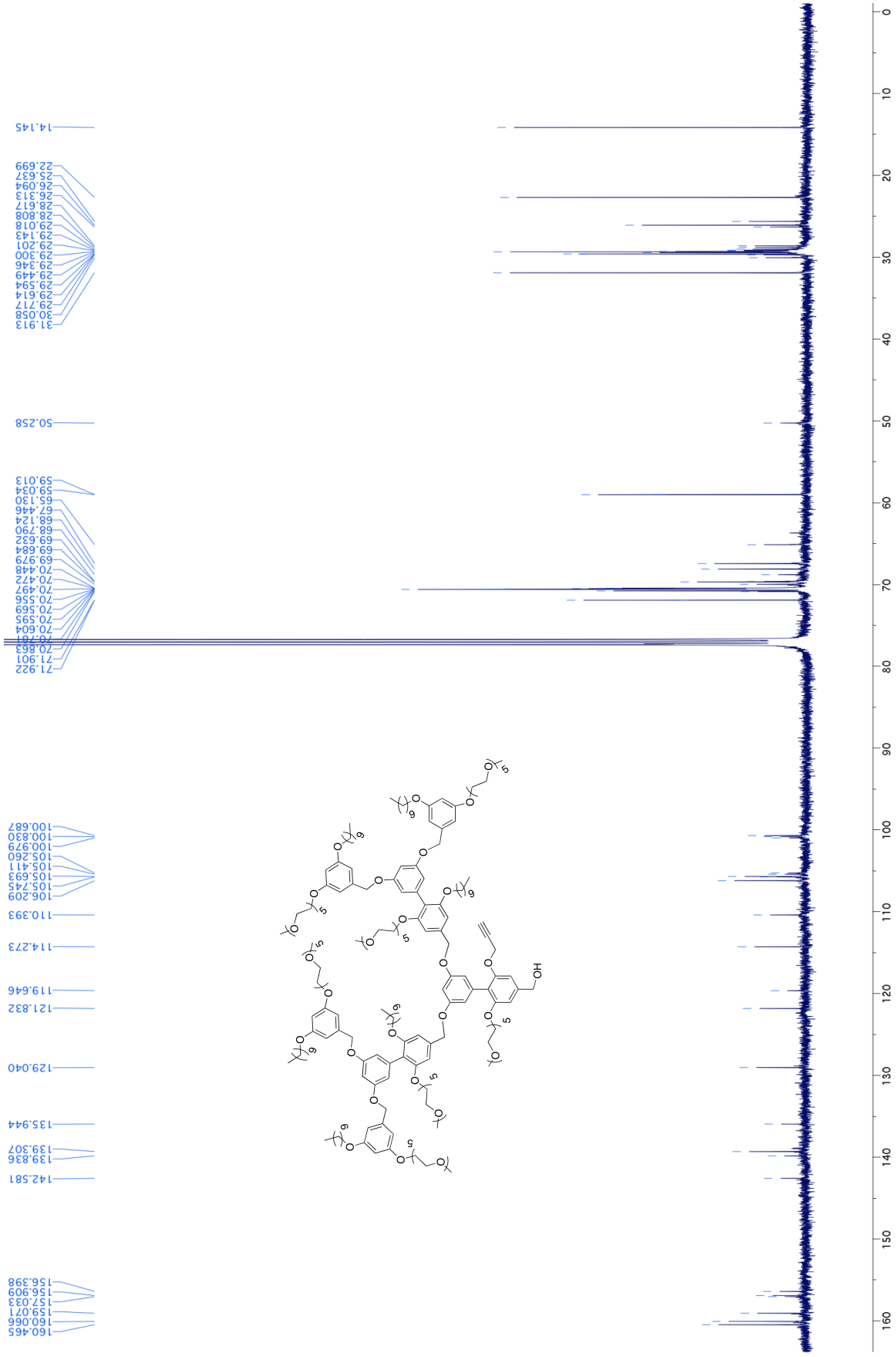
2
1
0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29.018
29.143
29.201
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29.346
29.449
29.594
29.614
29.717
30.058
31.913
50.258
59.013
59.034
65.130
67.446
68.124
68.790
69.632
69.684
69.979
70.448
70.472
70.497
70.556
70.595
70.604
70.863
71.901
71.922
100.687
100.830
100.979
105.260
105.411
105.693
105.745
106.209
110.393
114.273
119.646
121.832
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139.836
142.581
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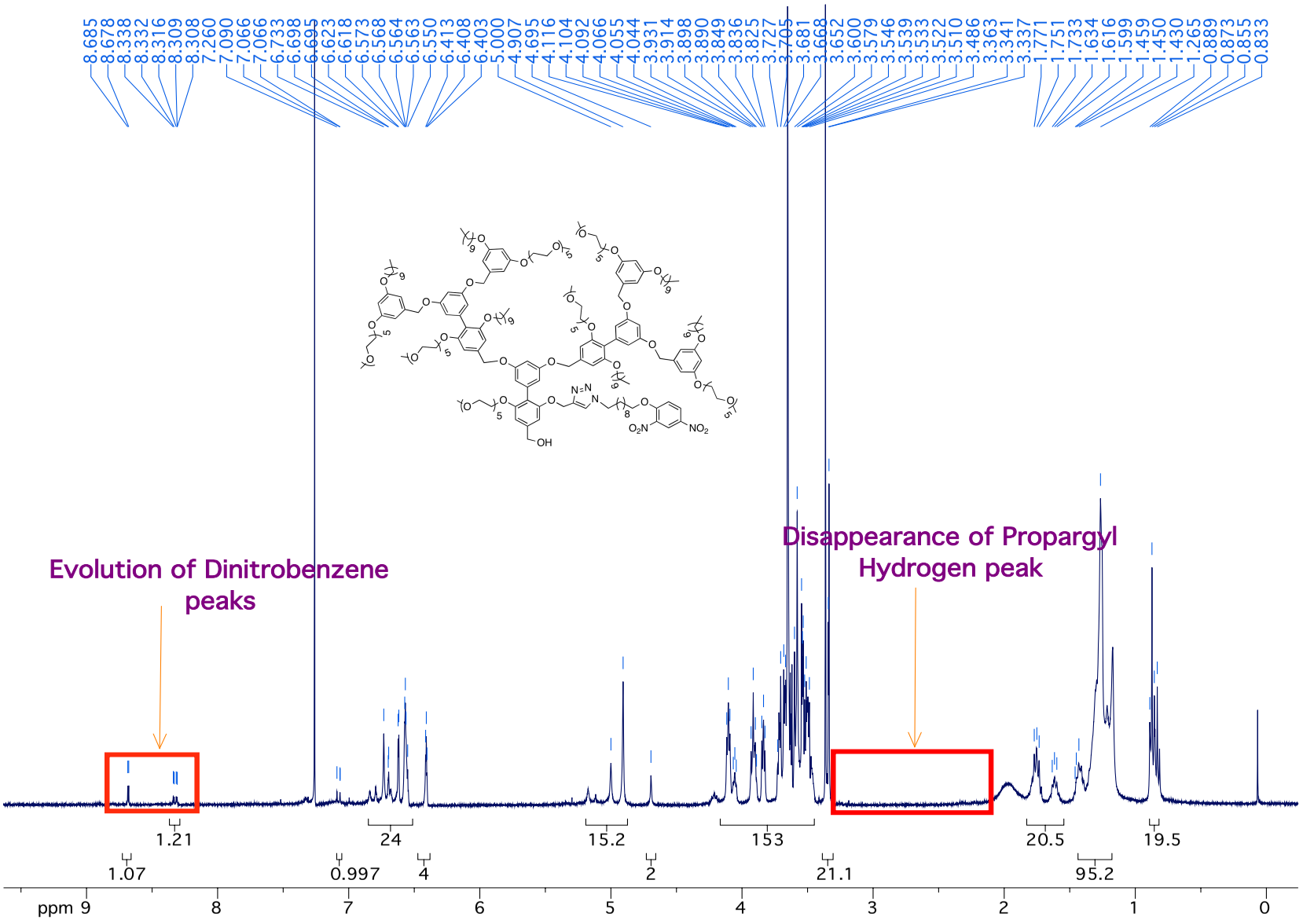
160.066
160.465
OH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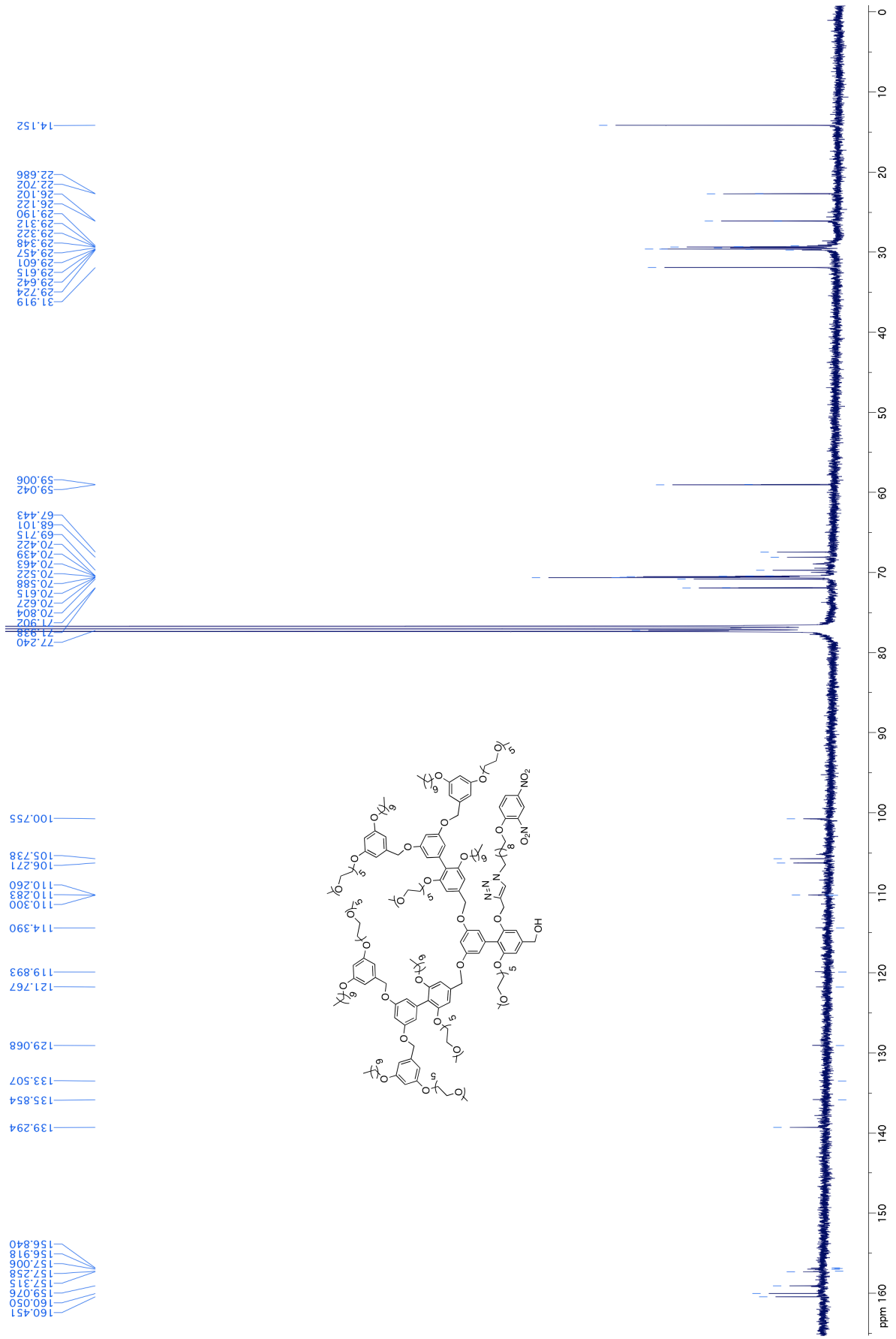
8.678
8.338
8.332
8.316
8.309
8.308
7.260
7.090
7.066
7.066
6.733
6.698
6.695
6.623
6.618
6.573
6.568
6.564
6.563
6.550
6.413
6.408
6.403
5.000
4.907
4.695
4.116
4.104
4.092
4.066
4.055
4.044
3.931
3.914
3.898
3.890
3.849
3.836
3.825
3.727
3.705
3.681
3.668
3.652
3.600
3.579
3.546
3.539
3.533
3.522
3.510
3.486
3.363
3.341
3.337
1.771
1.751
1.733
1.634
1.616
1.599
1.459
1.450
1.430
1.265
0.889
0.873
0.855
0.833
Evolution of Dinitrobenzene peaks
Disappearance of Propargyl Hydrogen peak
1.21
24
15.2
153
20.5
19.5
1.07
0.997
4
2
21.1
95.2
ppm 9
8
7
6
5
4
3
2
1
0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22.702
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26.122
29.190
29.312
29.322
29.348
29.457
29.601
29.615
29.642
29.724
31.919
59.042
59.006
67.443
68.101
69.715
70.422
70.439
70.463
70.522
70.588
70.615
70.627
70.804
71.902
71.938
77.240
100.755
105.738
106.271
110.260
110.283
110.300
114.390
119.893
121.767
129.068
133.507
135.854
139.294
156.840
156.918
157.006
157.258
157.315
159.076
160.050
160.451
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160